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## Theory of Dissociation Pressures of Some Gas Hydrates\*

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Dissociation pressures of some gas hydrates have been evaluated using the Lennard-Jones 12-6, 28-7, and Kihara potentials in the Lennard-Jones-Devonshire cell model. The Lennard-Jones 28-7 potential gives the least satisfactory results. The Lennard-Jones 12-6 potential works satisfactorily for the monatomic gases and  $\text{CH}_4$  but poorly for the rodlike molecules  $\text{C}_2\text{H}_6$ ,  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{C}_2\text{H}_4$ . This failure may be due to (i) distortions of the hydrate lattice, (ii) neglect of molecular shape and size in determining the cavity potential (iii) barrier to internal rotation of the molecule in its cavity. A crude model for the lattice shows that it is not distorted. The Kihara potential predicts better dissociation pressures for the hydrates of the rodlike molecules. Unlike the previously used Lennard-Jones 12-6 potential, it depends on the size and shape of the interacting molecules. The absence of lattice distortions, improved dissociation pressures through the use of the Kihara potential and the restriction of the motion of the solute molecule to around the center of a cavity makes a large barrier to rotation unlikely. A small barrier may still be present.

## INTRODUCTION

**C** LATHRATES are compounds which do not show ordinary chemical bonds. If water is crystallized slowly in the presence of some gases, a modified form of ice results with cavities which, for most cases, can trap one molecule each. These gas molecules stabilize the cavities.

The new structure is different from that of ordinary ice.<sup>1</sup> The gas-hydrate lattice of Structure I<sup>1</sup> contains almost spherical cavities of radii  $a_1=3.95$  Å and  $a_2=4.3$  Å. There are 20 and 24 water molecules, respectively, on the surface of these cavities.

Equilibrium between free gas molecules over the gas hydrates and the molecules in the force field of the lattice results when their chemical potentials are equal. This is the case at some definite external gas pressure, i.e., the equilibrium dissociation pressure of the gas hydrate.

Van der Waals and Platteuw<sup>2</sup> have derived the thermodynamic properties of gas hydrates from a simple model. They consider the gas molecule moving about in a spherical cage formed by the water molecules and apply the Lennard-Jones-Devonshire cell theory. The cell model is very appropriate here as the gas molecule is trapped in its cage and the surrounding molecules are fixed in their lattice positions.

The authors<sup>2</sup> use a Lennard-Jones 12-6 (LJ 12-6) potential for the force field in the cavity. The calculated dissociation pressures are good for the monatomic gases and the quasispherical molecule  $\text{CH}_4$  but are off by large factors for some nonspherical molecules, e.g.,  $\text{CO}_2$ ,  $\text{C}_2\text{H}_6$  (see Table I).

The internal partition functions of encaged molecules are taken to be equal to those of free gas molecules. The force field in the cavity is too weak to affect the energy levels which determine the electronic and internal vibrational partition functions. They<sup>2</sup> suggest that the poor agreement between calculated and observed dissociation pressures may be due to (1) hindered rotation of these rodlike molecules in their cavities, and (2) failure of the central field approximation in describing the interaction between a solute molecule and a molecule in the lattice.

In an attempt to remove this discrepancy between theory and experiment we have investigated three possible reasons<sup>3</sup> for the failure of the previous theory.

(i) The chemical potential of the lattice may not be independent of solute occupation. (ii) Shape and size of the encaged molecule cannot be neglected when evaluating the over-all cavity potential. (iii) Hindered rotation of the molecule in its cavity.

We discuss each of these in some detail and conclude: (1) the failure of the previous theory is partly due to the neglect of the shape and size effect of the solute molecule in determining the force field in the cavity; (2) to a good approximation the chemical potential of the lattice is independent of solute occupation of the cavity. Although we predict improved dissociation pressures by introducing the effect of shape and size of the molecule on the cavity potential, we cannot rule out a barrier to internal rotation of the molecule in its cavity, just on the basis of these improved dissociation pressures. The dissociation pressures are more sensitive to the parameters of the intermolecular potentials than are second virial coefficient data from which these parameters are determined. However these improved dissociation pressures, along with other considerations (see Sec. 2) make a barrier to internal rotation appear less likely as the cause for the failure of the previous theory.

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† Union Carbide Corporation Fellow 1962-63.

‡ Alfred P. Sloan Fellow.

<sup>1</sup> Hydrates crystallize in two structures, I or II. All the hydrates discussed in this paper belong to Structure I. For structural details see: M. von Stackelberg and H. R. Muller, *Z. Elektrochem.* **58**, 25 (1954).

<sup>2</sup> J. H. Van der Waals and J. C. Platteuw, *Advan. Chem. Phys.* **2**, 1 (1959).

<sup>3</sup> B. Alder, *Ann. Rev. Phys. Chem.* **12**, 195 (1961).

## 1. CELL MODEL

Reference 2 gives a good review of the theory and equations of the cell model which we use.

The final equations<sup>2</sup> for the dissociation pressure of a gas hydrate are

$$P_{\text{diss.}} = \frac{kT}{Q_1} \frac{y_1}{1-y_1} = \frac{kT}{Q_2} \frac{y_2}{1-y_2}, \quad (1)$$

where  $y_1$  and  $y_2$  are the occupation numbers for the cavities of radii  $a_1$  and  $a_2$ . These occupation numbers are proportional to the probability of finding a molecule in one of these cavities;  $Q_1$  and  $Q_2$  the configurational partition functions for a solute molecule in the cavity,

$$Q = 4\pi \int \exp[-w(r)/kT] r^2 dr, \quad (2)$$

where  $w(r)$  is the spherically symmetrical potential in the cavity, with  $r$  measured from center, and depends on the intermolecular potential we choose to describe the interaction between the engaged molecule and one of the water molecules in the lattice.

TABLE I. Dissociation pressures (atm).

Gas	$P_{\text{obs}}$	$P$ (LJ 12-6)	$P$ (LJ 28-7) (constants Table I)	$P$ (LJ 28-7) (constants Table II)	$P$ (Kihara)
Ar	95.5 <sup>a</sup>	95.5	516	95.0	
Kr	14.5	15.4	128	14.2	
Xe	1.15	1.0	12.0	0.65	
CH <sub>4</sub>	260	19.0	150.0	16.0	13.0 <sup>d</sup> 19.0 <sup>e</sup>
N <sub>2</sub>	140 <sup>b</sup>	90.0	530	72.0	115 115
O <sub>2</sub>	100 <sup>b</sup>	63.0	385.0	76.0	120
CO <sub>2</sub>	12.47 <sup>a</sup>	0.71 <sup>c</sup> 1.70	8.4 20.0		9.0
N <sub>2</sub> O	10.0	0.6 <sup>c</sup> 1.52	9.0 13.0		8.2
C <sub>2</sub> H <sub>6</sub>	5.20	1.1	13.0		8.4
C <sub>2</sub> H <sub>4</sub>	5.44	0.50	3.0		1.3 <sup>f</sup> 0.82 <sup>g</sup>
CF <sub>4</sub>	1	1.6	8.4	0.05	0.6

<sup>a</sup> J. H. van der Waals and J. C. Platteau; *Advan. Chem. Phys.* 2, 1 (1959).

<sup>b</sup> Calculated from data of A. van Cleff and G. A. Diepen *Rec. Trav. Chim.* 79, 582 (1960) and (private communication).

<sup>c</sup> See Table I.

<sup>d</sup> Spherical core  $\sigma=0.21$  (Table III).

<sup>e</sup> Spherical core  $\sigma=0.32$  (Table III).

<sup>f</sup>  $\rho_m=4.0$  (Table III).

<sup>g</sup>  $\rho_m=0.82$  (Table III).

<sup>h</sup> Calculated with parameters (d) of Table III. These replaced those of reference a. Danon and Pitzer's<sup>9</sup> parameters for CO<sub>2</sub> have an unreasonably large core.<sup>9</sup> Convergence in Eq. (14) is then slow.

$y_1$  and  $y_2$  satisfy<sup>2</sup>

$$\nu_1 \ln(1-y_1) + \nu_2 \ln(1-y_2) = -(\Delta\mu/kT), \quad (3)$$

where  $\nu_1$  and  $\nu_2$  are the numbers of cavities of radii  $a_1$  and  $a_2$  per lattice molecule, determined crystallographically.<sup>1</sup>  $\Delta\mu$  is the difference in chemical potential between the empty gas-hydrate lattice ( $\beta$ ) and ordinary ice ( $\alpha$ ), i.e.,

$$\Delta\mu = \mu^\beta - \mu^\alpha, \quad (4)$$

where  $Q_1$ ,  $Q_2$ , and  $\Delta\mu$ , along with Eqs. (1) and (3) fix the equilibrium dissociation pressures of a gas hydrate.

We first discuss the effect of  $\Delta\mu$  on the calculation of dissociation pressures and then go on to the evaluation of  $Q_1$  and  $Q_2$  where we will examine the use of the LJ 12-6, LJ 28-7, and Kihara potentials.

## 2. CHEMICAL POTENTIAL OF THE HYDRATE LATTICE

In their analysis van der Waals and Platteau<sup>2</sup> assumed the chemical potential of the lattice molecules to be independent of the mode of occupation of the cavities, i.e., the solute molecule does not interfere with the dynamics of the lattice. They then obtain Eq. (3) with  $\Delta\mu$  equal to the difference in chemical potential between the unperturbed gas-hydrate lattice ( $\beta$  ice) and ordinary ice ( $\alpha$  ice). We now give quantitatively approximate reasons justifying this assumption.

$\Delta\mu$  is determined by chemical analysis on a gas hydrate with molecules of dimensions such that they go only into the large cavities, i.e.,  $y_1=0$ ,  $y_2 \neq 0$ . The analysis then gives the concentration of the gas hydrate,  $\nu_2 y_2$ , i.e., the number of gas molecules per lattice molecule. With  $y_2$  known, Eq. (3) gives  $\Delta\mu = \mu^\beta - \mu^\alpha$ . From a study of bromine hydrate<sup>2</sup>  $\Delta\mu = 167$  cal/mole at  $T = 273^\circ\text{K}$ .

If there are no lattice distortions in the Br<sub>2</sub> hydrate or in any other of the hydrates, then this value of  $\Delta\mu$  is a constant for all the hydrates. If the lattice is distorted, Eq. (3) no longer holds. From a simple model, the possible lattice distortions appear to have a very small effect on the thermodynamic properties of the lattice.  $\Delta\mu$ , determined for the Br<sub>2</sub> hydrate, can then be used throughout all the calculations.

How does a solute molecule perturb the lattice? A gas molecule spends most of its time near the center of the cavity and is never further away than about 0.5-1 Å from this center. We show this quantitatively later (see Fig. 1). The molecules of interest, e.g., N<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, have bond lengths between 1 and 1.5 Å. The center of such a molecule is not further than 1 Å from the center of the cavity so that one end of it is never closer than 2.5-3 Å from the molecules in the cavity wall. The molecule then does not push the water molecule permanently out of its equilibrium position. However, it may affect the vibrational frequency of a lattice molecule about its equilibrium position. We now show that the lowest frequencies of the lattice molecule are

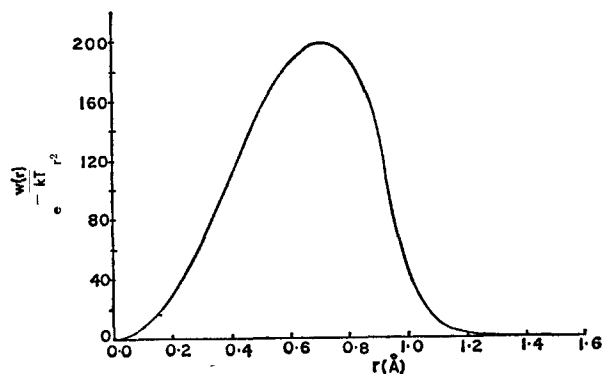


FIG. 1. Boltzmann probability factor vs  $r$  (distance from center of cavity),  $N_2$  hydrate. (LJ 12-6)

so much higher than those of the solute molecule, regarded as a "cavity oscillator," that they are unaffected to a good approximation, as assumed in Ref. 2.

The dispersion and repulsive forces between the lattice molecules and the solute give rise to the field in which the solute molecule moves in its cavity. We expand this cavity potential  $w(r)$  of the Lennard-Jones-Devonshire cell model<sup>4</sup> in terms of  $r/a$ , where  $r$  is the distance from the cavity and  $a$  is the cavity radius. For small  $r/a$

$$w(r) \equiv w(0) + (z\epsilon_0/a^2) [22(r_0/a)^{12} - 10(r_0/a)^6] r^2 + O(r^4), \quad (5)$$

where  $\epsilon_0$  and  $r_0$  are intermolecular parameters [see Eq. (8)];  $z$  is the number of lattice molecules in the wall of the cavity, and  $w(0)$  is the potential at the center of the cavity. The coefficient of  $r^2$  is equal to  $k/2$  of the three-dimensional harmonic oscillator potential

$$\tilde{w}(r) = w(0) + \frac{1}{2}kr^2, \quad (6)$$

and  $\tilde{w}(r)$  should be close to  $w(r)$  for small  $r/a$ .

The frequency of oscillation of this molecule is now

$$\nu_0 = 2\pi^{-1}(k/m)^{1/2}, \quad (7)$$

where  $m$  is the mass of the molecule. That the gas molecule oscillates with frequency  $\nu_0$  is only an approximation but our results do not depend critically on  $\nu_0$ . Typical  $\nu_0$  be between  $10^4$ – $10^5$  sec<sup>-1</sup>.

We now examine to what extent a perturbation by this frequency  $\nu_0$  can disturb the frequency spectrum of the empty hydrate lattice. This in turn determines how the thermodynamic properties of the lattice will change. The motion of the  $H_2O$  molecule in the ice lattice ( $\alpha$  or  $\beta$ ) is resolved approximately into three dependent vibrations<sup>5</sup>: (i) the translational vibration of the centers of gravity about their equilibrium positions, (ii) the rotational oscillations of the rigid

molecule, and (iii) the internal vibrations of individual water molecules.

The three modes correspond roughly to bands between 52–500 cm<sup>-1</sup> ( $2.10^{12}$ – $2.10^{13}$  sec<sup>-1</sup>); 800 cm<sup>-1</sup>; 1600 cm<sup>-1</sup> and higher, respectively.<sup>6</sup>

The frequencies  $2.10^{12}$  to  $2.10^{13}$  sec<sup>-1</sup> are the lowest in the frequency spectrum of the lattice. Comparing this frequency range with that of the solute molecule (or cavity oscillator in our model),  $10^4$  to  $10^5$  sec<sup>-1</sup>, we do not expect the frequency spectrum of the lattice to be affected, to a good approximation anyway. The thermodynamic properties of the lattice will then be independent of solute occupation. The spectroscopic bands quoted above refer to ordinary ice. These may change in going from the  $\alpha$  to  $\beta$  lattice, but certainly not enough to invalidate the order-of-magnitude argument above.

### 3. INTERMOLECULAR POTENTIAL AND FORCE FIELD IN THE CAVITY

We first select an intermolecular potential  $\Phi(r)$ , for the interaction between the gas molecule and one of the water molecules in the lattice. This interaction is then averaged over all neighboring  $H_2O$  molecules (nearest neighbors only) to obtain  $w(r)$ , the cavity potential.<sup>4</sup>

The motion of the molecule is pretty much confined to around the center of the cage. This can be seen from the following simple argument. The Boltzmann factor  $\exp[-w(r)/kT]r^2$  at  $r_1$  and  $r_2$  gives the relative probabilities of finding the molecule somewhere on shells of radii  $r_1$  and  $r_2$ . From Figs. 2 to 5 we see that the cavity potential  $w(r)$  rises sharply at about  $r=1$  Å. In Figs. 1 and 6 we plot  $\exp[-w(r)/kT]r^2$  vs  $r$ . The molecule then has a very small probability of being at  $r>1$  Å. (See Fig. 1.)

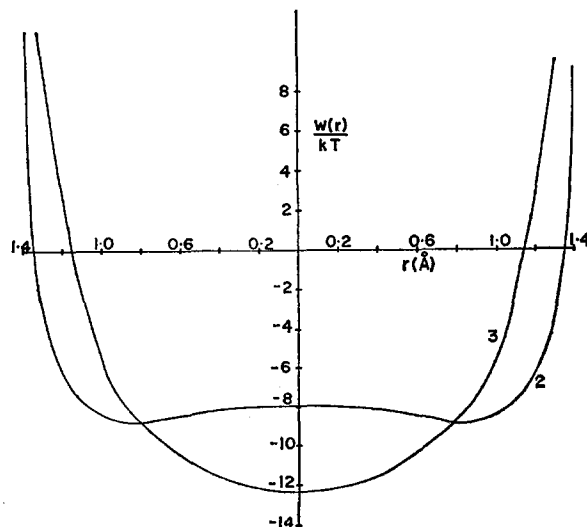


FIG. 2. Spherically symmetrical cavity potential  $w(r)$  for  $C_2H_6$  hydrate. 2: Kihara, 3: LJ 12-6.

<sup>6</sup> N. Ockman, *Advan. Phys.* **7**, 199 (1958).

<sup>4</sup> See for example R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, New York, 1939).

<sup>5</sup> R. W. Blue, *J. Chem. Phys.* **22**, 280 (1954).

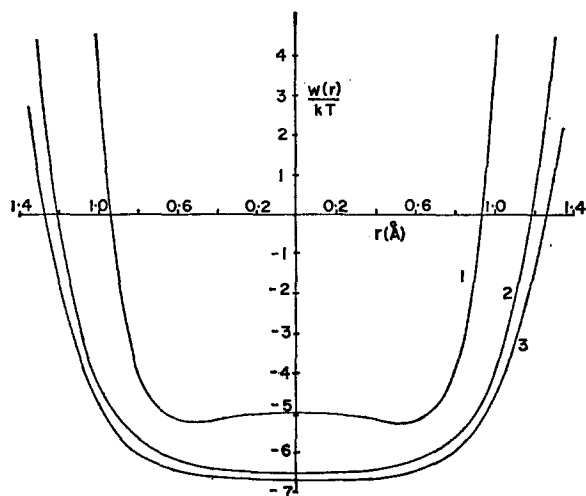


FIG. 3. Spherically symmetrical cavity potential  $w(r)$  for  $N_2$  hydrate (parameters as in Fig. 9). 1: LJ 28-7, 2: Kihara, 3: LJ 12-6.

Thus the motion of the molecule is quasivibration combined with rotation mainly around the center. This rotation is therefore not expected to be hindered. If, on the other hand, the cage potential had a much wider bowl, a molecule would have wandered too near the wall with a complicated tumbling motion. The result of this would show up as a strong change in the rotational partition function as compared to that of an unrestricted rotator. It then appears that no improvement in the theory of van der Waals and Platteeuw can be expected<sup>2,3</sup> from considering the restricted rotation of a diatomic molecule near the walls of the cavity, simply because the molecule is hardly ever there. Alder

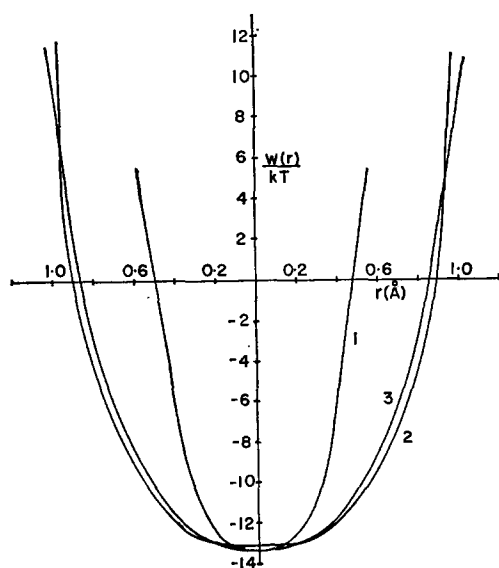


FIG. 4. Spherically symmetrical cavity potential  $w(r)$  for  $C_2H_4$  hydrate (parameters of Fig. 10). 1: LJ 28-7, 2: Kihara, 3: LJ 12-6.

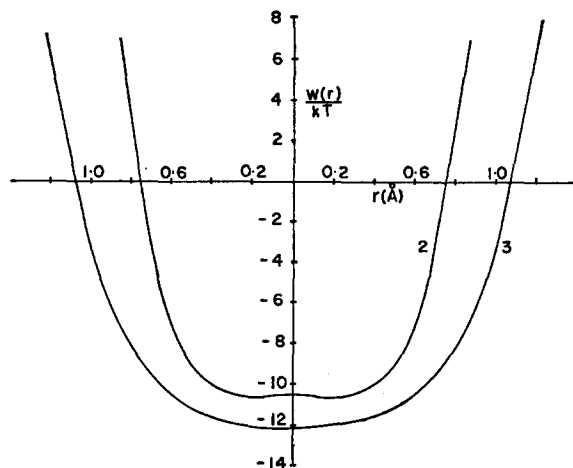


FIG. 5. Spherically symmetrical cavity potential  $w(r)$  for  $CO_2$  hydrate (parameters of Fig. 1). 2: Kihara, 3: LJ 12-6.

suggested that the previous theory may have been improved by this consideration.

We now examine a few intermolecular potentials and see if the discrepancy between the calculated and observed dissociation pressures is due to the inadequacy of the LJ 12-6 potential previously used.<sup>2</sup>

#### A. Lennard-Jones 12-6 Potential

Van der Waals and Platteeuw chose the LJ 12-6 potential,

$$\Phi(r) = \epsilon_0 \left[ \left( \frac{r_0}{r} \right)^{12} - 2 \left( \frac{r_0}{r} \right)^6 \right], \quad (8)$$

to describe the interactions in the cavity. This two-parameter potential, with  $\epsilon_0$  the potential minimum and  $r_0$  its position, does not depend on the shape and size of the interacting molecules.

With this potential they<sup>2</sup> obtain dissociation pressures in very good agreement with experiment for the monatomic gases xenon and krypton (see Table I). The dissociation pressure of argon hydrate is a special case since the empirical intermolecular potential parameters for the lattice molecule are chosen so that the

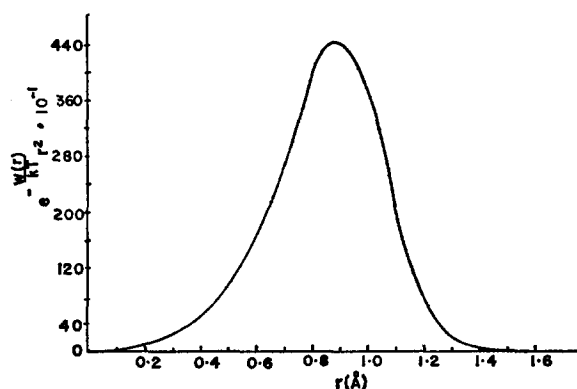


FIG. 6. Boltzmann probability factor vs  $r$  (distance from center of cavity),  $C_2H_6$  hydrate. (LJ 12-6)

calculated dissociation pressure agrees exactly with experiment. For  $\text{CH}_4$  hydrate the calculated dissociation pressure is less than the experimental value but still in satisfactory agreement ( $P_{\text{obs}} = 26$  atm;  $P_{\text{calc}} = 19$  atm). However, this potential (LJ 12-6) gives low dissociation pressures for the hydrates of  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , and even for the diatomic molecules  $\text{N}_2$  and  $\text{O}_2$ .

The interaction between a single water molecule in the lattice and one of these solute molecules, e.g.,  $\text{N}_2$ ,  $\text{C}_2\text{H}_6$ , and even  $\text{CH}_4$ , is noncentral; the noncentral part gets partly smoothed out when the potentials of all the  $\text{H}_2\text{O}$  molecules in the cell wall are added up, because the cell is very nearly spherical and the solute is confined pretty much to the center. Nevertheless, a more realistic potential would still take into account the shape-dependent effective size of the molecule after cell averaging. The resulting cell potential is then expected to have a narrower bowl which should lead to a smaller free volume and higher dissociation pressures [See Eq. (1)].

### B. Kihara Potential

Consider first the Kihara potential.<sup>7</sup> This potential assigns a core to each molecule. It therefore includes the effect of the finite size of the molecules on their interaction. This potential gives second virial coefficients in good agreement with experimental values<sup>7</sup> for many gases, e.g., those of rodlike molecules  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CO}_2$ , and has been successfully used in calculating cohesive energies and lattice constants for crystalline  $\text{N}_2$ ,  $\text{CO}_2$ , and  $\text{C}_2\text{H}_4$ .<sup>8</sup>

The core of a homopolar diatomic molecule is defined as the line segment between the nuclei. The core of other molecules may be specified in a similar way, e.g., the O-O distance in  $\text{CO}_2$ , the C-C distance in  $\text{C}_2\text{H}_4$  or  $\text{C}_2\text{H}_6$ , and a spherical core for  $\text{CH}_4$ .<sup>9</sup>

The energy of interaction  $\Phi(\rho)$  between two such molecules is then assumed to be of the LJ 12-6 form. However the argument of  $\Phi$  is now taken to be the shortest distance between molecular cores,

$$\Phi(\rho) = \epsilon [(\rho_m/\rho)^{12} - 2(\rho_m/\rho)^6], \quad (9)$$

with  $\epsilon$  the potential minimum and  $\rho_m$  its position.

We now consider two cases in particular (i) a molecule with a thin rod core of length  $l$ , e.g.,  $\text{N}_2$ ,  $\text{C}_2\text{H}_6$ , interacting with a point molecule of core length zero ( $l=0$ ), (ii) a molecule with a spherical core, e.g.,  $\text{CH}_4$  of radius  $a$  interacting with a "point molecule" ( $l=0$ ). The thin rod or spherical core molecule will represent the solute molecule in the cavity while the point molecule represents the water molecule in the lattice. The

water molecule is assigned zero core length for this reason: in its interaction with a solute molecule the oxygen atom of the water molecule plays the dominant role. As far as the nonpolar part of the potential is concerned we thus neglect the shape effects of  $\text{H}_2\text{O}$ 's. (Effect of water dipoles on the potential is examined in a later section.) To a good approximation atoms can be assigned a core  $l=0$ .<sup>10</sup> Also, all the intermolecular parameters for the lattice molecule are fixed empirically, i.e.,  $\epsilon_0$  and  $\rho_0$  for the LJ 12-6, and  $\epsilon_0$ ,  $\rho_m$ , and  $l$  for the Kihara potential. With this empirical procedure, along with the good agreement obtained for krypton and xenon hydrates with LJ 12-6 (for  $l=0$  the Kihara potential reduces to the LJ 12-6), we take  $l=0$  and fix  $\epsilon$  and  $\rho_m$  rather than fix all three parameters.

We now obtain the equations of the Lennard-Jones-Devonshire cell theory for these model systems. Consider a thin rod of length  $l$  with center at a distance  $R$  from a point (the lattice molecule). The shortest distance between molecular cores  $\rho$  is the distance from this external point to a point on the surface of a hemisphere which the near end of the thin rod molecule sweeps out as it rotates. With  $\psi$  and  $\phi$  orienting the rod,  $b=1/2$ , we average Eq. (9):

$$\langle \Phi(R, b) \rangle_{\text{av}} = \langle \Phi(R, \psi, \phi, b) \rangle_{\text{av}} \\ = \epsilon (\rho_m^{12} \langle 1/\rho^{12} \rangle_{\text{av}} - 2\rho_m^6 \langle 1/\rho^6 \rangle_{\text{av}}), \quad (10)$$

$$\left\langle \frac{1}{\rho^n} \right\rangle_{\text{av}} = \frac{1}{2\pi} \int_0^\pi \int_0^\pi \sin\psi d\psi d\phi (R^2 + b^2)^{-n/2} \\ \times [1 - 2Rb(R^2 + b^2)^{-1} \sin\psi \sin\phi]^{-n/2}. \quad (11)$$

Expand the last term in the integrand and integrate term by term

$$\langle \Phi(R, b) \rangle_{\text{av}} = \epsilon \sum_{n=0}^\infty b^n [\rho_m^{12} (\alpha_n/R^{n+12}) - \rho_m^6 (\beta_n/R^{n+6})], \quad (12)$$

where  $\alpha_n$  and  $\beta_n$  are constants. The series is infinite but converges rapidly for  $b \ll R$ . The first term in the series has the ordinary LJ 12-6 form.

Equation (12) is a quasispherical approximation, for we have removed all angular dependence. It does depend, however, on the molecular size through  $b = \frac{1}{2}l$ , and on shape through its derivation.

We now look at such a rodlike molecule located a distance  $r$  from the center of a gas hydrate cavity. Equation (12) describes its interaction with one of the lattice molecules. Summing this interaction in the usual manner<sup>4</sup> we obtain the spherically symmetrical potential  $w(r)$ ,

$$w(r) = \frac{Z\epsilon}{4\pi} \int_0^{2\pi} \int_0^\pi \Phi(R, b) \sin\theta d\theta d\phi, \quad (13)$$

<sup>7</sup> T. Kihara, J. Phys. Soc. (Japan) **6**, 289 (1951).

<sup>8</sup> T. Kihara, J. Phys. Soc. (Japan) **14**, 247 (1959); **16**, 627 (1961).

<sup>9</sup> A tetrahedral core is more obvious, but for  $\text{CH}_4$  a spherical core is satisfactory. See F. Danon and K. S. Pitzer, J. Chem. Phys. **36**, 425 (1962).

<sup>10</sup> For argon see T. Kihara and S. Koba, J. Phys. Soc. (Japan) **9**, 608 (1954).

$\theta$  and  $\phi$  now locate the molecule in the cavity and  $z$  is the number of nearest neighbors.

Substituting Eq. (12) into Eq. (13) we obtain

$$w(r) = \frac{Z\epsilon}{2} \sum_{n=0}^{\infty} (b/a)^n \left[ f_n \frac{\mu_n(y)}{\alpha^4} - \frac{g_n \lambda_n(y)}{\alpha^2} \right], \quad (14)$$

where  $f_n$  and  $g_n$  are constants,  $y = (r/a)^2$ , and  $\alpha = (a/\rho_m)^{1/3}$ .

$$\mu_n(y) = 1/y^{\frac{1}{2}} \left[ \frac{1}{(1-y^{\frac{1}{2}})^{n+10}} - \frac{1}{(1+y^{\frac{1}{2}})^{n+10}} \right], \quad (15)$$

$$\lambda_n(y) = 1/y^{\frac{1}{2}} \left[ \frac{1}{(1-y^{\frac{1}{2}})^{n+4}} - \frac{1}{(1+y^{\frac{1}{2}})^{n+4}} \right]. \quad (16)$$

This is a convenient series in  $b/a$  (ratio of half-core length to cavity radius) for the spherically symmetrical potential in the cavity and reduces to that obtained by starting from the LJ 12-6 potential if  $l=0$ .

For the case of a solute molecule with a spherical core of radius  $c$ , we obtain, instead of Eqs. (12) and (13),

$$\Phi(R, c) = \epsilon \left[ \frac{\rho_m^{12}}{(R-c)^{12}} - \frac{2\rho_m^6}{(R-c)^6} \right], \quad (17)$$

$$w(r) = \frac{Z\epsilon}{2} \left( \frac{\rho_m}{10a^{11}r} \left\{ \frac{1}{[1-(r/a)-(c/a)]^{10}} - \frac{1}{[1+(r/a)-(c/a)]^{10}} \right\} + \frac{\rho_m^{12}c}{11a^{12}r} \right. \\ \times \left\{ \frac{1}{[1-(r/a)-(c/a)]^{11}} - \frac{1}{[1+(r/a)-(c/a)]^{11}} \right\} \\ \left. - \frac{\rho_m^6}{2a^6r} \left\{ \frac{1}{[1-(r/a)-(c/a)]^4} - \frac{1}{[1+(r/a)-(c/a)]^4} \right\} \right. \\ \left. - \frac{2\rho_m^6c}{5a^6r} \left\{ \frac{1}{[1-(r/a)-(c/a)]^5} - \frac{1}{[1+(r/a)-(c/a)]^5} \right\} \right). \quad (18)$$

Putting Eq. (14) or Eq. (18) into Eq. (2), we evaluate first the configurational partition function and then the dissociation pressures for the gas hydrates of  $N_2$ ,  $O_2$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $CO_2$ ,  $N_2O$ , and  $CH_4$ .

### C. LENNARD-JONES 28-7 POTENTIAL

Hamann and Lambert<sup>11</sup> have shown that a Lennard-Jones 28-7 potential suitably describes the interaction between two quasispherical molecules:

$$\Phi(r) = \epsilon_m/3[(r_0/r)^{28} - 4(r_0/r)^7]. \quad (19)$$

They obtained the energy of interaction between two such quasispherical molecules by summing the individual atomic interaction energies and averaging

the resulting potential over all orientations. The interaction between two atoms, one in each of the molecules, is described by the LJ 12-6 potential, Eq. (8). The resulting expression is not suitable for computations but a LJ 28-7 potential is a good fit to the curve for the total interaction. The equations of the cell theory for this potential are given in reference 11.

So far our model for the solute molecule, e.g.,  $N_2$  is a freely rotating one that spends most of its time close to the center of the cavity. In its interaction with a lattice molecule a rotating dumbbell 3-5 Å away from the lattice, should appear quasispherical. We then use this quasispherical LJ 28-7 potential to describe the force field in the cavity. The resulting dissociation pressures have only a qualitative meaning for two major reasons. We discuss the first below and the second in the next section.

The averaging used to obtain a quasispherical approximation starting from the Kihara potential is conceptually equivalent to that used by Hamann and Lambert.<sup>11</sup> Our averaging is done explicitly for the two cases, (1) a rodlike molecule interacting with a point molecule, (2) a "spherical-core" molecule interacting with a point molecule. The LJ 28-7 potential was derived explicitly for the interaction between two quasispherical molecules. In the cavity a point molecule interacts with a quasispherical one. The quasispherical potential, Eq. (12), is therefore better suited to the interactions in the gas hydrate cavities.

The LJ 28-7 potential will be steeper than the quasispherical approximation, Eq. (12). We look at a quasispherical molecule as made up of a central atom joined to some peripheral atoms. In the interaction of two such quasispherical molecules the contribution from the interaction between peripheral atoms in different molecules is the steepest. For a given separation between centers of these molecules, the peripheral atoms approach one another quite closely.

It should be mentioned that the averaging used in deriving the LJ 28-7 potential<sup>11</sup> from individual atomic interactions is not strictly correct. In averaging the interaction between a central atom, A, in one quasispherical molecule, say  $AB_4$ , and the peripheral atoms  $B_1 \cdots B_4$  in the other, only the interaction between central atom A and one of the peripheral atoms  $B_1 \cdots B_4$  can be averaged independently of molecular geometry. Fixing one of the "B" atoms  $B_1(b_1\theta_1\varphi_1)$  ( $b$  = bond length), completely determines the location of the other three shell atoms  $B_2, B_3, B_4$ . The integration over  $\varphi_1, \theta_1$  is independent but those over, e.g.,  $(\theta_2\varphi_2), (\theta_4\varphi_4)$  are not since, e.g.,  $\theta_2$  is a function of  $(\theta_1\varphi_1)$ . We do not have eight independent variables  $(\theta_1 \cdots \varphi_4)$ . In their integrations Hamann and Lambert treat all the angular variables as independent. The correct averaging can be carried out with the use of Gegenbauer polynomials.<sup>12</sup> However, the two methods,

<sup>11</sup> S. D. Hamann and J. A. Lambert, Australian J. Chem. 7, 1 (1954).

<sup>12</sup> See, for example, O. Sinanoğlu, J. Chem. Phys. 30, 850 (1959) and R. Balescu, Physica 22, 223 (1956).

TABLE II. Potential parameters for calculating lattice-solute interaction by the geometric mean and hard sphere approximation for LJ 12-6.<sup>a</sup>

Gas	$r_0$ (Å)	$\epsilon_0/k$ (°K)
Ar	3.83	119.5
Kr	4.13	166.7
Xe	4.57	225.3
CH <sub>4</sub>	4.28	142.7
O <sub>2</sub>	3.88	118.0
N <sub>2</sub>	4.15	95.1
CO <sub>2</sub>	4.57	205
	5.04	189
C <sub>2</sub> H <sub>4</sub>	5.08	199
C <sub>2</sub> H <sub>6</sub>	4.44	243
N <sub>2</sub> O <sup>b</sup>	4.67	205
	5.15	189
CF <sub>4</sub>	5.28	152
H <sub>2</sub> O <sup>c</sup>	2.80	167

<sup>a</sup> J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

<sup>b</sup> See the section on parameters for intermolecular potentials, this article.

<sup>c</sup> J. H. van der Waals and J. C. Platteuw, *Advan. Chem. Phys.* **2**, (1959).

one including the geometry of the molecule the other neglecting it are equivalent in our case. This is only so because of the spherical symmetry of the enclosure in which the molecule is located.

#### 4. PARAMETERS FOR THE INTERMOLECULAR POTENTIALS

The calculated dissociation pressures are very sensitive to the intermolecular force constants used. There are different values of these parameters reported even for the rare gases which have been most studied, e.g.,  $\epsilon_0/k=124^\circ\text{K}$ ,  $r_0=3.84$  Å,  $\epsilon_0/k=116$ ,  $r_0=3.90$  Å from viscosity data and  $\epsilon/k=120^\circ\text{K}$ ,  $r_0=3.83$  Å;  $\epsilon/k=122^\circ\text{K}$ ,  $r_0=3.82$  Å, from second virial coefficient data for argon with LJ 12-6 potential.<sup>13</sup> This range of values for the intermolecular force constants becomes larger for bigger molecules (see Tables II and III). This is partly due to: (i) inadequacy of the LJ 12-6 potential to fit experimental second virial coefficient data over a wide temperature range with one set of parameters; and (ii)  $B(T)$ , second virial coefficient data, are too insensitive to small changes in the empirical parameters of the potential used to calculate them.

In Tables II to IV we list the parameters used in calculating the dissociation pressures. We first discuss those of the Kihara potential in Table III. The values  $\rho_m=3.40$  Å;  $\epsilon/k=132^\circ\text{K}$  and  $l=1.19$  Å for N<sub>2</sub> given by Danon and Pitzer<sup>9</sup> are those obtained when the

quadrupole moment of N<sub>2</sub> is neglected. They are close to those given by Kihara. Pitzer<sup>9</sup> also gives values of these parameters when quadrupole-quadrupole interactions are considered. We do not consider such effects as quadrupole-dipole or quadrupole-quadrupole interactions. These are known to be small effects.<sup>8,14</sup>

Four sets of parameters are listed for CO<sub>2</sub>. The set  $\rho_m=3.70$  Å;  $\epsilon/k=279^\circ\text{K}$   $l=2.2$  Å was replaced by the new values  $\rho_m=3.36$ ,  $\epsilon/k=309^\circ\text{K}$   $l=2.3$  Å by Kihara so as to fit more recent second virial coefficient data.<sup>7,8</sup> We use only the new set in calculating the dissociation pressure of CO<sub>2</sub> hydrate. Neglecting quadrupole-quadrupole interactions Danon and Pitzer obtain parameters  $\rho_m=2.72$  Å,  $\epsilon/k=400^\circ\text{K}$  and  $l=3.29$  Å. A core length  $l=3.29$  Å is unreasonably large (the O-O distance in CO<sub>2</sub> is 2.30 Å), but even with this large core agreement is obtained with second virial coefficient data. Including quadrupole-quadrupole interactions, Danon and Pitzer obtain  $\rho_m=3.42$  Å,  $\epsilon/k=270^\circ\text{K}$   $l=1.73$  Å even though the core length is now reasonable, such a change in parameters due to quadrupole-quadrupole interactions is unexpected since these interactions are known to be small.<sup>13,14</sup>

TABLE III. Potential parameters for lattice-solute molecule by geometric-mean and hard-sphere approximation for Kihara potential.

Gas	$l$ (Å) or $a$ (Å) (core length or radius)	$\rho_m$ (Å)	$\epsilon/k$ (°K)
N <sub>2</sub>	1.094 <sup>a</sup> 1.190 <sup>b</sup>	3.47 3.40	124 132
O <sub>2</sub>	1.10 <sup>c</sup>	3.14	153
CO <sub>2</sub>	2.20 <sup>a</sup> 2.30 <sup>d</sup> 3.29 <sup>b</sup>	3.70 3.36 2.72	279 309 400
C <sub>2</sub> H <sub>4</sub>	1.34 <sup>a</sup> 1.33 <sup>c</sup>	4.0 4.2	266 256
C <sub>2</sub> H <sub>6</sub>	1.54 <sup>f</sup>	2.59	609
N <sub>2</sub> O	2.31 <sup>e</sup>	3.40	309
CH <sub>4</sub>	0.21 <sup>b</sup> 0.32 <sup>b</sup> 0.30 <sup>i</sup>	3.81 3.35 3.39	178 205 204
CF <sub>4</sub>	0.72 <sup>i</sup>	3.22	291

<sup>a</sup> T. Kihara, *J. Phys. Soc. (Japan)* **6**, 289 (1951).

<sup>b</sup> F. Danon and K. S. Pitzer, *J. Chem. Phys.* **36**, 425 (1952).

<sup>c</sup> T. Kihara and S. Koba, *J. Phys. Soc. (Japan)* **9**, 608 (1954).

<sup>d</sup> T. Kihara, *Rev. Mod. Phys.* **25**, 831 (1953). These parameters replaced those in reference a for CO<sub>2</sub>.

<sup>e</sup> S. Koba, *J. Phys. Soc. (Japan)* **16**, 627 (1961).

<sup>f</sup> Present work.

<sup>g</sup> Obtained by adjusting those of CO<sub>2</sub> (reference d) with theorem of corresponding states.

<sup>h</sup> Present work.

<sup>i</sup> D. R. Doulsen, *Symposium on Thermophysical Properties* (Academic Press Inc., New York, 1962).

<sup>13</sup> J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

<sup>14</sup> B. J. Castle, L. Jansen, and J. M. Dawson, *J. Chem. Phys.* **24**, 1078 (1956).



For CH<sub>4</sub> Pitzer and Danon obtain  $\rho_m = 3.82 \text{ \AA}$ ,  $\epsilon/k = 175^\circ\text{K}$ , a (radius of spherical core)  $= 0.21 \text{ \AA}$ . This core appears to be too small as a core of this radius does not contain much of the polarizable electron density. With a tetrahedral core formed by the mid-points of the C-H bonds of CH<sub>4</sub> Kihara obtains good agreement with second virial coefficient data.<sup>15</sup> As an improved spherical core we choose a sphere inscribed in the cube formed by this tetrahedral core.

For the LJ 28-7 potential we use two sets of parameters. First the constants were chosen to be the same as those of the LJ 12-6. The true parameters for the LJ 28-7 will certainly be different from those of the LJ 12-6. The dissociation pressures calculated with these parameters have only a qualitative meaning showing the effect of the shape of the potential well on dissociation pressures since these dissociation pressures are quite sensitive to minimum parameters ( $r_0$ ,  $\epsilon_0$ ).

The second set of constants is those obtained by fitting the second virial coefficients to the theoretical LJ 28-7 curve<sup>11</sup> (Table IV). The potential well  $\epsilon/k$  so obtained is about twice as deep as those of the LJ 12-6 or Kihara potentials. Such a well depth is unrealistic, particularly for the monatomic gases and the diatomics N<sub>2</sub>, O<sub>2</sub>, for which any change from the LJ 12-6 well depth cannot be large. These values of  $\epsilon_m$  for the LJ 28-7 potential come out so large for the following reason. The parameters  $r_m$  and  $\epsilon/k$  were determined by fitting the theoretical curve for  $B(T)$  vs  $\log(kT/\epsilon)$  at different  $r_m$  to a graph of the experimental  $B(T)$  vs  $T$ . For the first six gases listed in Table IV this fitting was done mainly around the Boyle temperature.

TABLE IV. Potential parameters for calculating lattice-solute interaction by the geometric mean and hard sphere approximation. (LJ 28-7).<sup>a</sup>

Gas	$r_m$ (Å)	$\epsilon_m/k$ (°K)
Ar <sup>a</sup>	3.36	240
Kr	3.48	340
Xe	3.88	470
CH <sub>4</sub>	3.63	310
N <sub>2</sub>	3.64	190
O <sub>2</sub>	3.42	240
CO	3.69	200
CF <sub>4</sub>	4.63	315
H <sub>2</sub> O <sup>b</sup>	2.70	338

<sup>a</sup> S. D. Hamann and J. A. Lambert, Australian J. Chem. 7, 1 (1954).

<sup>b</sup> Present work.

<sup>15</sup> Figure 1 of reference 9 shows Kihara's  $B(T)$  second virial coefficients vs  $T$  lying below the experimental values. This refers to a core identical to the nuclear framework of CH<sub>4</sub>. Kihara<sup>8</sup> replaced this core by the one above, giving good agreement with experiment.

Second virial coefficients around the Boyle temperature for gases Argon, O<sub>2</sub>, N<sub>2</sub> ( $T \approx 300^\circ\text{K}$ ) are determined mainly by the attractive part of the potential. Out in the attractive region, e.g.,  $r = 2r_0$ , the total potential  $\Phi(r)$  is given mainly by the second terms of Eqs. (8) and (19)

$$\text{LJ 12-6} \quad \Phi(r) = -2\epsilon_0(r_0/r)^6, \quad (20)$$

$$\text{LJ 28-7} \quad \Phi(r) = -\frac{4}{3}\epsilon_m(r_m/r)^7. \quad (21)$$

But in this region an inverse 6 potential  $c/r^6$  should be close to the true potential-energy curve for a point molecule and approximately so for N<sub>2</sub>, O<sub>2</sub> or CH<sub>4</sub>. A satisfactory potential should go over to an inverse 6 potential at large enough  $r$ . The Kihara potential satisfies this condition, but the LJ 28-7 does not. This wrong "asymptotic" behavior affects  $\epsilon_m$  as follows: at  $r \approx 2r_0$  choose  $\epsilon_m$  so that

$$\Phi(\text{LJ 28-7}) \sim \Phi(\text{LJ 12-6}). \quad (22)$$

For Argon and O<sub>2</sub>,  $\epsilon_m \approx 1.8\epsilon_0$ . This is only an order of magnitude argument but agrees well with the values given in Tables I and II, where  $\epsilon_m \approx 2\epsilon_0$ .

The most convenient method of fixing parameters  $r_m$  and  $\epsilon/k$  for a lattice molecule is that used by van der Waals and Platteuw.<sup>2</sup> They take  $r_0$  equal to the van der Waals radius of the oxygen atom, 2.8 Å. This is close enough to the  $r_0$  value of the Stockmayer potential for H<sub>2</sub>O-H<sub>2</sub>O interaction  $r_0 = 2.82 \text{ \AA}$ .<sup>13</sup> ( $\epsilon/k$ )<sub>H<sub>2</sub>O</sub> is then chosen so as to obtain agreement between calculated and experimental dissociation pressures for argon hydrate using the LJ 12-6 potential. These values of  $r_0$  and  $\epsilon_0/k$  for the lattice molecule are then used in the calculations on the other gas hydrates along with combining rules for parameters, i.e., the hard-sphere  $r_{AB} = (r_A + r_B)/2$  and geometric-mean  $\epsilon_{AB} = (\epsilon_A \epsilon_B)^{1/2}$  approximations.

For the Kihara potential the lattice molecule is assigned zero core length ( $l=0$ ). The Kihara potential then reduces to the LJ 12-6 potential and hence the parameters of the lattice molecule are the same in the two potentials. This equivalence for  $l=0$  and the combining rules  $\rho_{AB} = (\rho_A + \rho_B)/2$  and  $\epsilon_{AB} = (\epsilon_A \epsilon_B)^{1/2}$  have been shown to be true for the Kihara potential.<sup>10</sup>

For the LJ 28-7 potential we selected  $\epsilon_m$  (LJ 28-7)  $\sim 2$  (LJ 12-6) for the lattice molecule since this is the case for the parameters listed by Hamann and Lambert<sup>11</sup> (Tables II and IV). ( $r_m$ )<sub>lattice</sub> is then fixed so as to obtain agreement between calculated and experimental dissociation pressures of the argon hydrate.

Van der Waals and Platteuw<sup>2</sup> include only the repulsive and dispersion forces in the interaction between solute and lattice molecules. All the solute molecules have zero dipole moment but the lattice molecule has a dipole moment  $\mu_b = 1.83.10^{-18}$  esu. For the interaction between a nonpolar molecule, polarizability  $\alpha_A$ , and a

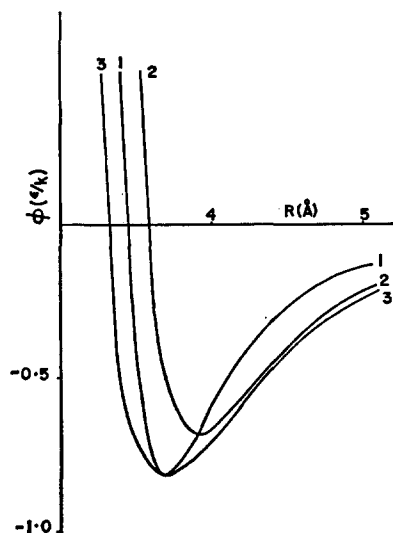


FIG. 7. Potential-energy curve for  $\text{CO}_2$ -single lattice molecule interaction. Well depth is  $\epsilon/k$  of Kihara potential. 1: LJ 28-7 (parameters of Table I), 2: Kihara ( $\rho_m = 3.36$  Å,  $\epsilon/k = 309^\circ\text{K}$ ), 3: LJ 12-6 ( $r_0 = 4.57$  Å,  $\epsilon/k = 205^\circ\text{K}$ ).

polar molecule, dipole moment  $\mu_b$  we can write<sup>13</sup>

$$\Phi(r) = (\epsilon_a \epsilon_b)^{1/2} [(r_{ab}/r)^{12} - 2(r_{ab}/r)^6] - \alpha_A \mu_b^2 / r^6, \quad (23)$$

$$r_{ab} = (r_a + r_b)/2, \quad (24)$$

with  $r_a$  and  $r_b$  the position of the potential minima and  $\epsilon_a$ ,  $\epsilon_b$  their depths in the ordinary LJ 12-6 potential [Eq. (8)]. Equation (23) can be put into the 12-6 form<sup>13</sup>

$$\Phi(r) = (\epsilon_{ab}') [(r_{ab}/r)^{12} - 2(r_{ab}/r)^6], \quad (24)$$

$$\epsilon_{ab}' = \eta^2 (\epsilon_a \epsilon_b)^{1/2}, \quad (25)$$

$$r_{ab}' = (1/\eta^{1/6}) r_{ab}, \quad (26)$$

$$\eta = 1 + \alpha_A \mu_b^2 / [2r_a^3 r_b^3 (\epsilon_a \epsilon_b)^{1/2}]. \quad (27)$$

The parameter that van der Waals determined empirically is  $\epsilon_{ab}'$  and not  $\epsilon_{ab} = (\epsilon_a \epsilon_b)^{1/2}$ . For argon hydrate they<sup>2</sup> chose  $r_a = 3.83$  Å. With  $r_b$  (lattice molecule) = 2.8 Å,  $r_{ab} = 3.3$  Å. Again this quantity is not  $r_{ab}$  but  $r_{ab}'$ . Interpreting these parameters correctly we have recalculated some dissociation pressures. The dissociation pressures calculated in these two approximations will be in better agreement the closer its  $\eta$  value [Eq. (27)] is to  $\eta$  (argon). Ethane has a polarizability  $\alpha = 4.40 \times 10^{-24}$  cm<sup>3</sup> compared to  $\alpha$  (argon) =  $1.63 \times 10^{-24}$  cm<sup>3</sup>;  $\alpha(\text{N}_2) = 1.74 \times 10^{-24}$  cm<sup>3</sup>;  $\alpha(\text{O}_2) = 1.57 \times 10^{-24}$  cm<sup>3</sup>;  $\alpha(\text{CO}_2) = 2.65 \times 10^{-24}$  cm<sup>3</sup>. The new dissociation pressure for ethane is 0.89 atm compared to 1.1 atm given by van der Waals.<sup>2</sup> Such a small change is expected since the third term [Eq. (23)] is only about 8% of the second and assuming  $\eta(\text{C}_2\text{H}_6) \approx \eta(\text{Argon})$  already takes part of this into account.

## 5. RESULTS

Table I summarizes the results obtained with the three different potentials. The cell theory with the

LJ 12-6 potential predicts good dissociation pressures for krypton and xenon. Empirical lattice parameters are fixed to make the calculated and experimental dissociation pressures for argon hydrate agree exactly. The LJ 12-6 potential gives a reasonable result for  $\text{CH}_4$  hydrate, but the calculated dissociation pressure is below the experimental ( $P_{\text{calc}} = 19$  atm,  $P_{\text{obs}} = 26$  atm). The experimental dissociation pressure for  $\text{CF}_4$  is unreliable, reported to be approximately 1 atm.<sup>2</sup> However the LJ 12-6 gives increasingly poor results for the hydrates of  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{C}_2\text{H}_6$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{C}_2\text{H}_4$ , the ratio  $P_{\text{obs}}/P_{\text{calc}}$  increasing from 1.5 to 10.

With the Kihara potential we obtain improved dissociation pressures for the rodlike molecules  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{C}_2\text{H}_6$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{C}_2\text{H}_4$  the improvement being least for  $\text{C}_2\text{H}_4$ . With the exception of  $\text{C}_2\text{H}_4$  the ratio  $P_{\text{obs}}/P_{\text{calc}}$  now lies between 1.2 and 0.6. The Kihara potential curve for one of these molecules interacting with a lattice molecule has a narrower bowl than does the LJ 12-6 (see Figs. 7 to 10). The cavity potential,  $w(r)$ , of the Kihara potential lies above that of the LJ 12-6. This is a result of the repulsive forces between the molecules becoming important at a smaller distance  $R$ , than the LJ 12-6 predicts. Figure 2,  $w(r)$  for ethane hydrate, shows that the "point" molecule can wander about 0.7 Å away from the center before seeing the same potential that the rodlike molecule sees while still at the center. The Kihara cavity potential  $w(r)$  for ethylene hydrate is not much different from that of the LJ 12-6. Both potentials predict low dissociation pressures. The intermolecular parameters for  $\text{C}_2\text{H}_4$  are less reliable than those of  $\text{C}_2\text{H}_6$ . Those of  $\text{C}_2\text{H}_4$  are determined from second virial coefficient data over a rather narrow temperature range. Van der Waals and Platteau suggested that the low dissociation pressure predicted for  $\text{C}_2\text{H}_4$  hydrate may be due to anisotropic forces caused by the  $\pi$  electrons. Such anisotropic con-

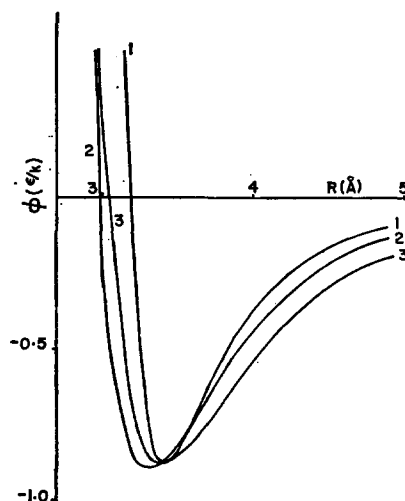


FIG. 8. Potential-energy curve for  $\text{O}_2$ -single lattice molecule interaction. Well depth is  $\epsilon/k$  of Kihara potential. 1: LJ 28-7 (parameters of Table I), 2: Kihara, 3: LJ 12-6.

tributions are essentially cancelled out when the potentials of all the  $\text{H}_2\text{O}$  molecules in the cell wall are added up. (See the section on the LJ 12-6 potential.)

The LJ 12-6 potential does not consider the shape and size of molecules in describing their interactions. We first see the consequence of this on the dissociation pressure of  $\text{CH}_4$  hydrate, which falls below the experimental value (Table IV). With the spherical core of reference 9, the Kihara potential gives a dissociation pressure  $p=13$  atm, which is lower than the LJ 12-6 value of 19 atm. We have mentioned that Danon and Pitzer's<sup>9</sup> core,  $a=0.21$  Å, appears too small and we selected a core of radius  $a=0.32$  Å.<sup>16</sup> With these new parameters the dissociation pressure comes out equal to 19 atm (LJ 12-6 value also 19 atm). We do not expect a large size effect for  $\text{CH}_4$ . With the larger core,  $a=0.32$ , Å we obtain a higher dissociation pressure,

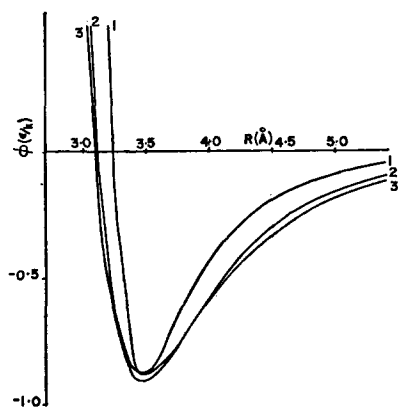


FIG. 9. Potential-energy curve for  $\text{N}_2$ -single lattice molecule interaction. Well depth is  $\epsilon/k$  of Kihara potential. 1: LJ 28-7 (parameters of Table I), 2: Kihara ( $\rho_m=3.47$  Å,  $\epsilon/k=124^\circ\text{K}$ ), 3: LJ 12-6.

$p=19$  atm. The size effect shows up quite clearly in this case.

There is some uncertainty in the observed dissociation pressure of  $\text{CF}_4$  hydrate<sup>2</sup> (approximate value = 1 atm). The Kihara potential predicts  $p=0.6$  atm and the LJ 12-6,  $p=1.6$  atm.

The dissociation pressures calculated with the LJ 28-7 potential are the least satisfactory. For the case where we used the same parameters as in the LJ 12-6 potential the pressures are too high. The dissociation pressures are sensitive to the potential parameters ( $\epsilon/k$ ,  $r_m$ ) and the true parameters for the LJ 28-7 potential are certainly not equal to those of the LJ 12-6 (see Tables I and II). These pressures then have only a qualitative meaning: the effect of narrowing the potential bowl on dissociation pressures, i.e., going from LJ 12-6 to LJ 28-7.

With parameters given by Hamann and Lambert,<sup>11</sup>

<sup>16</sup> This choice turns out to be quite close to 0.30 Å, Table III, obtained by D. R. Douslin, *Symposium on Thermophysical Properties* (Academic Press, Inc., New York, 1962).

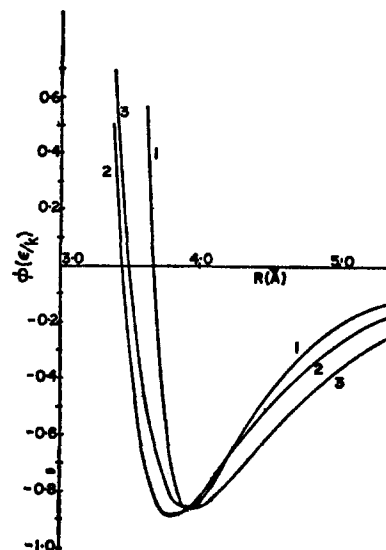


FIG. 10. Potential-energy curve for  $\text{C}_2\text{H}_4$ -single lattice molecule interaction. Well depth is  $\epsilon/k$  of Kihara potential. 1: LJ 28-7 (parameters of Table I), 2: Kihara ( $\rho_m=4.0$  Å;  $\epsilon/k=266^\circ\text{K}$ ), 3: LJ 12-6.

i.e., the set derived by fitting second virial coefficients to the theoretical 28-7 curve, the dissociation pressures are too low. The depth of the potential well  $\epsilon/k$  in this case is about twice that of the LJ 12-6 or Kihara potentials and seem to be in error.<sup>17</sup> These large values of  $\epsilon/k$  lead to larger free volume integrals and hence lower dissociation pressures.

In order of steepness of the potential bowls we have (see Figs. 7 to 10): (1) LJ 28-7, (2) Kihara, (3) LJ 12-6. We have already given reasons why the LJ 28-7 potential is expected to have too narrow a bowl for the interaction between a quasispherical molecule and a "point" molecule.

Table V gives the occupation numbers  $y_1$  and  $y_2$ , [Eq. (1)], for some hydrates. These numbers are proportional to the probability of finding a molecule in cavities of radii  $a_1$  and  $a_2$ .

Calculated dissociation pressures are sensitive to the

TABLE V. Occupation numbers ( $y_1$ ,  $y_2$ ) for some hydrates.

Hydrate	$y_1$		$y_2$	
	LJ 12-6 <sup>a</sup>	Kihara	LJ 12-6 <sup>a</sup>	Kihara
$\text{O}_2$	0.821	0.821	0.839	0.839
$\text{N}_2$	0.810	0.843	0.845	0.843
$\text{CO}_2$	0.786	0.528	0.861	0.879
$\text{C}_2\text{H}_4$	0.523	0.740	0.879	0.852
$\text{C}_2\text{H}_6$	0.837	0.860	0.827	0.818

<sup>a</sup> J. H. van der Waals and J. C. Platteuw, *Advan. Chem. Phys.* 2, 1 (1959).

<sup>17</sup> See the section, "Parameters for Intermolecular Potentials," This article.

TABLE VI. Effect of varying the empirical parameters ( $r_0$ ,  $\epsilon_0/k$ ) of water molecules in the lattice on calculated dissociation pressures (LJ 12-6).

Gas	$r_0$ changed from 2.8 to 2.7 Å	No change in ( $r_0$ , $\epsilon_0$ )	$\epsilon_0/k$ changed from 167 to 187°K
N <sub>2</sub>	110 atm	90	65
C <sub>2</sub> H <sub>6</sub>	1.61	1.0	0.6
C <sub>2</sub> H <sub>4</sub>	0.58	0.58	0.24

empirical parameters of the intermolecular potentials. Those of the solute gases are determined from second virial coefficient data.  $\epsilon/k$  and  $r_0$  for the water molecule in the lattice are chosen so as to obtain agreement between calculated and observed dissociation pressures of argon hydrate. In Table VI, we show the effect of small changes in these  $\epsilon/k$  and  $r_0$  (lattice parameters) on dissociation pressures. A 4% decrease in  $r_0$  of the lattice changes the dissociation pressures by factors of 1.2 to 1.6 while a 13% increase in  $\epsilon_0/k$  does likewise by a factor of 1/2 to 2/3.

## 6. DISCUSSION AND CONCLUSIONS

With dissociation pressures as a criterion we conclude: (1) LJ 12-6 potential is satisfactory for the hydrates of the monatomic gases and CH<sub>4</sub>; (2) for the rodlike molecules, N<sub>2</sub>, O<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, N<sub>2</sub>O, CO<sub>2</sub>, the Kihara potential is more suitable; (3) the LJ 28-7 is the least satisfactory whether (a) we use the same parameters for the LJ 28-7 potential as in the LJ 12-6, or (b) the experimental well depths<sup>11</sup>  $\epsilon/k$  obtained separately which are unrealistically large. The LJ 28-7 potential is steeper than the actual potential curve for the interaction of a quasisphepherical molecule and a point molecule would be.

The effect of molecular size shows up strongly in the dissociation pressures of C<sub>2</sub>H<sub>6</sub>, CO<sub>2</sub>, N<sub>2</sub>O, etc. With a more realistic model for the interacting molecules the Kihara potential yields an improved force field for the gas hydrate cavities. From Figs. 7 to 10 the bowl of

the Kihara potential lies below that of the LJ 28-7 (with same parameters as the LJ 12-6) but above that of the LJ 12-6. The Kihara potential then gives a smaller configurational partition function than the LJ 12-6 and hence higher dissociation pressures.

The failure of previous theory<sup>2</sup> had been attributed to two reasons<sup>2,3</sup> (i) failure of the central field point molecule approximation for the cavity potential, and (ii) restricted rotation of the molecules in their cavities. We also investigated (iii) the effect of possible distortions of the lattice by the solute molecule. One sees that: (1) to a good approximation, lattice distortions are not significant, (2) the molecule is confined pretty much to the center of the cage and does not collide with the wall (i.e., no hindered rotation or "tumbling"). A small barrier to internal rotation may still be present but such a barrier would be observable at low temperatures.<sup>18</sup> With the molecule around the center of the cavity the main improvement comes from the use of the Kihara potential which remedies the LJ 12-6 potential by taking into account the size and shape of the molecule. This gives improved dissociation pressures. The dissociation pressures are sensitive to intermolecular parameters; nevertheless, a comparison of the Kihara and LJ 12-6 potentials is meaningful because the experimental parameters of both potentials have the same reliability. They are determined from the same second virial coefficient data. Therefore with the molecule being mainly around the center of the cavity, which is nearly spherical, a large barrier to internal rotation is very unlikely.

With some care, the calculation of dissociation pressures can be used as a sensitive test for selecting intermolecular force constants. Table VI shows the sensitive dependence of dissociation pressures on force constants. The parameters of this paper may be very useful in estimating thermodynamic properties of gaseous mixtures, e.g., C<sub>2</sub>H<sub>6</sub>-H<sub>2</sub>O.

<sup>18</sup> N. G. Parsonage and L. A. K. Staveley, *Mol. Phys.* **3**, 59 (1960) found no barrier in quinol clathrate of CH<sub>4</sub> hydrate since (i) lattices of both clathrates are hydrogen-bonded structures (ii) cavities have same radii ( $a=3.95$  Å).